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(71) Applicant: Montedison S.p.A., 31, Foro Buonaparte, I-20121 Milan (IT)

(72) Inventor: Marchionni, Giuseppe, 8, via Vallisneri, I-20133 Milan (IT)
Inventor: Viola, Gian Tommaso, 13, via Pignocchi, I-48015 Cervia Ravenna (IT)

(74) Representative: Zumstein, Fritz, Dr. et al, Dr. F. Zumstein Dr. E. Assmann Dipl.-Ing. F. Klingseisen Bräuhausstrasse 4, D-8000 München 2 (DE)

(54) Bifunctional and monofunctional perfluoropolyethers having brominated end groups and a controlled molecular weight.

(57) New mono- and bi-functional perfluoropolyethers comprising repeating units chosen from amongst (C_2F_4O), (CF_2O) and ($\underset{(CF_3)}{C}FO$), statistically distributed along the chain, having a controlled molecular weight and brominated end groups, prepared starting from the product of the photochemical oxidation of C_2F_4, and/or C_3F_6, having different peroxide oxygen contents, and subsequent treatment in liquid phase with bromine, at temperatures ranging from -40° to 130°C in the presence of ultraviolet radiations.

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MONTEDISON S.p.A.
Milan / Italy

"BIFUNCTIONAL AND MONOFUNCTIONAL PERFLUOROPOLYETHERS HAVING BROMINATED END GROUPS AND A CONTROLLED MOLECULAR WEIGHT"

BACKGROUND OF THE INVENTION.

This invention relates to new perfluoropolyethers having a Br atom bound to one or both the end groups of the chain.

More in particular this invention relates to new mono- or bifunctional perfluoropolyethers having a controlled molecular weight and consisting of units chosen from amongst (C_2F_4O) (CF_2O) (C_3F_6O) and $(\underset{\substack{|\\CF_3}}{CFO})$ statistically distributed along the perfluoropolyether chain.

A further object of the present invention is that of pro-

viding a process for preparing the abovesaid perfluoropolyethers with brominated end groups and having a controlled molecular weight by a method which is easily practicable on a commercial scale and is capable of providing high yields of brominated product.

It is known that the reaction of oxygen with tetrafluoroethylene and/or perfluoropropene, carried out at a low temperature in the presence of UV radiations and in an inert solution, generally a fully fluorinated compound or a chlorofluorinated compound, leads to a perfluoroether product having a peroxide oxygen content which varies as a function of the operative conditions under which the photooxidation has been effected.

The process and the peroxidic products are disclosed for example in GB 1,226,566 and 1,104,482.

The thermal decomposition of the peroxide which is carried out in order to remove peroxide bridges, leads to high molecular weight perfluoropolyethers containing neutral end groups of the type $-CF_3$, $-CF_2CF_3$ and acylic end groups of the type $-OCF_2COF$.

Actually, the thermal decomposition reaction of the peroxide product for providing the neutral perfluoropolyether gives rise to radicals of the type $R_fO.CF_2$ (Rf being a perfluoroether chain) which react with one another, thus leading always to perfluoropolyethers having a high and non-controlled molecular weight.

Generally, in order to obtain low molecular weight perfluoropolyethers, the thermal decomposition of the peroxidized perfluoroether product is accomplished in the presence of chain end groups.

The resulting perfluoropolyethers are not completely neutral and may contain small fractions with end groups deriving from the chain end group employed.

Furthermore, by operating in this manner, it is not possible to correctly control the molecular weight of the perfluoropolyethers free from peroxide bridges.

The decompositions of the peroxidized precursors is usually carried out by means of a heat treatment carried out in a wide temperature range, generally from about 100°C up to high temperatures, preferably from 180° to 250°C.

THE PRESENT INVENTION.

It has now surprisingly been found that it is possible to prepare new or bifunctional perfluoropolyethers with brominated end groups and a controlled molecular weight and with high yields if the treatment of the peroxidized precursor, having a proper peroxide oxygen content as a function of the desired molecular weight of the final product, is conducted unter suitable conditions.

The new perfluoropolyehters with brominated end groups according to the invention have the general formula:

$$\text{(I)}\quad A\text{-}(OC_3F_6)_m\text{-}\left(\begin{matrix}OCF\\ |\\ CF_3\end{matrix}\right)_n\text{-}(OCF_2)_p\text{-}(OC_2F_4)_r\text{-}O\text{-}B$$

wherein m, n, p and r are integers from 0 to 50, m+n+p+r being at least 2, and wherein A and B, equal or different between them, are end groups, chosen from the class:

$$-CF_2X,\ -CF_2CF_2X,\ -\underset{\displaystyle CF_3}{\underset{|}{C}}FX,\ -CF_2\underset{\displaystyle CF_3}{\underset{|}{C}}FX,\ -COF,\ -CF_2COF,\ -\underset{\displaystyle CF_3}{\underset{|}{C}}FCOF$$

wherein X is Br or F, and at least one of the groups A and B contains a bromine atom.

The perfluoro-oxyalkylene units of general formula (I) are statistically distributed along the perfluoropolyether chain.

The process according to the invention for preparing mono- or bifunctional perfluoropolyethers with high yields, consists in subjecting a peroxidized perfluoropolyether, obtained from the photooxidation of tetrafluoroethylene and/or perfluoropropene, having a predeterminated peroxide oxygen content, to photolysis with UV radiations, in liquid phase, in the presence of bromine at temperatures ranging from -40° to 130°C, either or not in the presence of a completely fluorinated or chlorofluorinated inert solvent, the liquid reaction medium being fully saturated with bromine.

The product resulting from the photooxidation which contains peroxide bridges, can be utilized as such if the peroxide oxygen content is already at the value suitable for obtaining the desired molecular weight of the final brominated perfluoropolyether.

Should the peroxidized precursor have a higher peroxide oxygen content than desired, then it is subjected to thermal treatments according to conventional techniques such as the ones described in the above-mentioned British patent.

The term peroxide oxygen content (P.O.) means the amount in grams of activated oxygen referred to 100 grams of perfluoropolyether.

The average molecular weight of the brominated perfluoropolyether is directly related to the peroxide oxygen content of the starting perfluoropolyether.

In fact, in correspondence of the peroxidic bridges, during the bromination according to the invention, occurs a cleavage of the perfluoropolyether chain: consequently the reduction of the average molecular weight is proportional to the peroxidic bridges in the chain.

The solvent utilized in the bromination reaction is any fully fluorinated or, as an alternative, chlorofluorinated compound which is inert in the reaction conditions and does not contain unsaturations.

As solvents, useful to the purpose there may be cited, for example, the perfluorocarbon or the fluorocarbons.

To prepare bromine-saturated solution, it is generally operated having the bromine present as a botton body in the reaction apparatus.

The preferred reaction temperature is in the range of from 60° to 120°C, more preferably from 90° to 110° C.

In fact, by operating under the above-cited conditions it is possible to obtain very high yields of brominated perfluoropolyethers; therefore it could be assumed that the radicals which form from the peroxide decomposition, completely react with bromine, providing only end groups of the type $-CF_2Br$, or $-\underset{CF_3}{\underset{|}{C}}FBr$.

If there is only one peroxidic bridge in the starting perfluoropolyether chain, the obtained products shall be prevailing by monobrominated compound. If there are many peroxidic bridges in the starting perfluoropolyether chain, the obtained products shall be prevailing formed by dibrominated compounds.

If it is operated at higher temperatures than 130°C, the perfluoropolyethers according to the invention are still obtained, however, they contain only very low percentages of brominated, in particular of dibrominated perfluoropolyethers.

By the process of the present invention it is possible to prepare both high molecular weight perfluorobrominated compounds and low molecular weight perfluorobrominated compounds, depending on the peroxide oxygen content of the starting precursor, or by acting on the temperature at which the photolysis of the initial peroxide is carried out.

In fact, the high molecular weights are obtainable by operating at temperatures from -40° to 80°C, while low molecular weight brominated perfluoropolyethers are obtainable in a temperature range of from 80° to 130°C.

The brominated products according to the invention can be obtained also by carrying out the bromination in the high temperature range, in absence of U.V. radiations. In this case, however, the yield of brominated perfluoropolyether is very low and such a process could not have any interest from a technical point of view.

Furthermore it has been found that by the simple heat treatment it is not possible to obtain perfluoropolyethers with a controlled molecular weight depending on the peroxide content of the starting perfluoropolyether.

The process indicated hereinbefore permits to overcome all the abovesaid drawbacks. In fact, the new brominated perfluoropolyethers of the invention are obtained by an utmostly simplified process with very high yields and with a molecular weight regulated as a function of the peroxide content of the

starting peroxidized perfluoropolyether.

The following examples are given merely to illustrate the present invention without limiting, however, the scope and applicative modalities thereof.

Example 1

Into a cylindrical photochemical reactor having a maximum capacity of 300 ml, with an optical path of 0,5 cm, equipped with a coaxial quartz sheath for housing a mercury vapour lamp type Hanau TQ 150 or a noble gas discharge lamp, for example a Xenon lamp type PEK INC. X-75, equipped with a magnetic stirrer, a reflux dropping device, a CO_2 trap and a thermoregulation system for both the reactor and the sheath system, there were introduced 430 g of perfluoropolyether obtained from tetrafluoroethylene having a peroxidic oxygen (P.O.) content of 1.04% by weight, a viscosity of 9500 cSt (at 20°c), an average molecular weight of 39930 and a m/n ratio, determined through NMR (^{19}F) analysis, equal to 0,8. 5 ml of bromine were added, the whole was mixed and the temperature was brought to about 100°C. Subsequently, after switching on of the lamp, 20 ml of bromine were added during the test which lasted 14 hours. At the conclusion of the test, the reaction mass was discharged into a flask and bromine was distilled under vacuum.

Obtained were 390 g of a product having a viscosity of 20 cST and practically free from P.O., and having average molecular weight (PM) of 3550 such product exhibiting, on NMR (^{19}F) analysis, the following structure:

$$BrF_2C\text{-}O(C_2F_4O)_m(CF_2O)_n\text{-}CF_2Br$$

with a m/n ratio = 0,8, analogous with the one of the starting

product.

The chemical shifts of the brominated end groups (δ, ppm; $CFCl_3$) were, respectively:

$-OCF_2OCF_2Br$	-19.9 ppm
$-OCF_2CF_2OCF_2Br$	-18.4 ppm

The product yield in brominated products was equal to 96% with respect to 4% of neutral product of formula:

$$RO-(C_2F_4O)_n-(CF_2O)-R'$$

where R und R', equal or different from each other, may be $-CF_3$ and $-CF_2CF_3$.

Example 2

Into the photochemical reactor of example 1 there were introduced 125.3 g of fluoropolyether obtained from tetrafluoroethylene having a P.O. of 1.04% by weight and a viscosity of 9500 cSt, along with 280 g of the throughly fluorinated solvent 1,2-perfluorodimethyl cyclobutane.

After mixing of the mass, 2 ml of bromine were added and the temperature was brought to 0°C.

Subsequently, after switching on of the lamp, further 6 ml of bromine were added during the test which lasted 20 hours. At the conclusion of the test, the reaction mass was discharged into a flask and the bromine as well as the solvent were distilled under vacuum.

Obtained were 109 g of product having a viscosity of 32 cSt and being practically free from P. O., having PM of 4630 such product exhibiting, on NMR (^{19}F) analysis, the same structure

as the dibrominated product of example 1.

Example 3

Into a 200-cc flask equipped with a stirrer, a thermometer, a cooler and a dropping device, 100 g of perfluoropolyether obtained from tetrafluoroethylene, having a P.O. equal to 1,2% by weight, viscosity of 5300 and PM of 31300 were introduced. The reactor temperature was brought to 150°C and 8 ml of bromine were added at regular intervals during 5 hours: subsequently the temperature was brought to 210°C and the mixture was refluxed during additional 5 hours. At the end of the test, bromine was removed under vacuum, so obtaining 79 g of a product having a viscosity of 17 cST, and PM of 4300 which, on NMR (^{19}F) analysis, revealed to have practically the same structure as the dibrominated product abtained in example 1, but with a yield equal to 5% with respect to 95% of completely fluorinatd neutral product.

Example 4

120 g of perfluoropolyether of example 3 obtained from tetrafluoroethylene, having a P.O. equal to 1,2% by weight, were introduced into the flask of example 3. The reactor temperature was brought to 150°C and 8 ml of Br_2 were added during the 5-hour test; subsequently the temperature was raised to 180°C and the whole was allowed to react during additional 5 hours. At the conclusion of the test, bromine was removed under vacuum and 93 g of a product having a viscosity of 21 cSt were obtained; such product, subjected to NMR (^{19}F) analysis, proved to have practically the same structure as the dibrominated product obtained in example 1, but with a yield equl to 4,5% with respect to 95.5% of completely fluorinated neutral product.

Example 5

420 g of perfluoropolyether obtained from tetrafluoroethylene

with a P.O. of 1.5% by weight, a viscosity of 14400 cSt and a molecular weight of 46200 were introduced into a photochemical reactor similar to the one described in example 1.

After switching on of the lamp and maintaining a temperature of 100°C, 25 ml of bromine were added during 18 hours. At the conclusion of the test there were obtained 345 g of a product having a viscosity of 7 cSt and PM of 2600 with a yield of dibrominated product equal to 96.5% besides 3.5% of neutral product.

Example 6

Under the same conditions of examples 5 and using the same perfluoropolyether, but at a temperature of 60°C, there were obtained 350 g of a product having a viscosity of 45 cSt and an anverage molecular weight of 5250.

The % amount of dibrominated product was higher than 85%.

Example 7

Under the same conditions and using the same perfluoropolyether of example 5, but operating at a temperature of 120°C, there were obtained 330 g of a perfluoropolyether with a viscosity of 10 cSt and a molecular weight of 3000; in this case the dibrominated product amount was equal to 74%.

Example 8

A peroxide perfluoropolyether obtained by photochemical oxidation of tetrafluoroethylene, having a mean molecular weight of 24500 and a peroxide content equal to 0,9% by weight, was reduced by means of a thermal treatment at a temperature of 160°C during 5 hours till obtaining a product having an average molecular weight of 18000 and a peroxide

oxygen content equal to 0.35% by weight.

400 g of such product were placed into a photochemical reactor similar to the one described in example 1 and were irradiated in the presence of Br_2 (7 ml) during 10 hours at a temperature of 100°C.

After removal of Br_2 under vacuum, there were obtained 380 g of a product having a viscosity of 65 cSt and a content of products with brominated functionalities equal to 95% by weight.

Example 9

Into the photochemical reactor of example 1 there were introduced 400 g of perfluorpolyether obtained from C_3F_6, having a peroxidic oxygen content (P.O.) of 0,7% by weight and a molecular weight of 2550 (~~osmometric~~ measure).

Subsequently 10 g bromine are added and the temperature is raised to 100°C. After switching on the lamp further bromine was added during the test (20 g during 15 hours). At the end of the test, the reaction mass was discharged into a flask and residual bromine was distilled under vacuum.

The obtained product (395 g) showed an average molecular weight of 1220, was practically free from P.O. and contained brominated end groups $-CF_2Br$ and $-\underset{\displaystyle CF_3}{\underset{|}{C}}FBr$ in amount equal to a brominated end group for each perfluotopolyether chain, the other end group being of the type:

$$-OCF_3, \quad -O\underset{\displaystyle CF_3}{\underset{|}{C}}F-COF \quad \text{or} \quad -O-C\!\!\begin{array}{l}\nearrow O\\ \searrow F\end{array}$$

Example 10

Into a photochemical reactor having capacity of 1000 ml and on

optical path of 2 cm equipped with coaxial quart sheats for housin .a mercury vapour lamp type Marian TQ 150 with traps and thermoregulation system suitable for maintaining the temperature at -40°C, were introduced 1000 g of perfluo opropene. After switching on the lamp, a mixture $O_2 + C_2F_4$ in molar ratio of 192 l/h (measured at atmospheric pressure). After 150' the lamp was switched off and 380 g of a perfluoropolyether having P.O. equal to 3.23% and viscosity of 1064 cSt (20°C).

From the NMR analysis it came out that the structure consists of C_3F_5O units randomly alternated with CF_2CF_2O and CF_2O units and of peroxidic units.

The reduction of the peroxidic oxygen content was obtained by subjecting the product to the irradiation of a U.V.lamp in the reactor used in example 1 and maintaining the temperature at 0°C.

After 18 hours, the P.O.content was 1,1% and the molecular weight of the product was 2780.

In the same reactor was carried out the bromination reaction at 100°C, by introducing 10 g bromine at the beginning and then further 40 g during the following 30 hours. Peroxidic oxygen was completely eliminated.

After removal of excess bromine, 340 g of perfluoropolyether were obtained, of average molecular weight 1050, having brominated end groups $-\underset{\displaystyle CF_3}{\underset{|}{C}}FBr$ and $-CF_2BR$

near neutral end groups of the type $-OCF_3$ and acid end group of the type $-O\underset{\displaystyle CF_3}{\underset{|}{C}}F-COF$ and $-O-C\begin{smallmatrix}\nearrow O\\ \searrow F\end{smallmatrix}$.

The functionality of the product, expressed as ratio between

brominated end groups and number of perfluoropolyether chains is 1.3.

WHAT IS CLAIMED IS:

1) Perfluoropolyethers of general formula:

$$A-(OC_3F_6)_m-\left(\begin{array}{c}OCF\\ |\\ CF_3\end{array}\right)_n-(OCF_2)_p-(OC_2F_4)_r-O-B$$

wherein m, n, r and p are integers from 0 to 50, m+n+r+p being at least 2, and wherein A and B, equal or different between them, are end groups chosen from amongst:

$$-CF_2X, -CF_2CF_2X, -\underset{\displaystyle CF_3}{\underset{|}{C}}FX, -CF_2\underset{\displaystyle CF_3}{\underset{|}{C}}FX, -COF, -CF_2COF, -\underset{\displaystyle CF_3}{\underset{|}{C}}FCOF$$

wherein X is fluorine or bromine, and at least one of the groups A and B contains a bromine atom, the perfluoro-oxyalkylene units being distributed randomly along the perfluoropolyether chain.

2) A process for preparing the perfluoropolyethers according to claim 1, consisting in photolysing with UV radiations the product obtained from the photochemical oxidation of C_2F_4 and/or C_3F_6 in the presence of bromine at a temperature ranging from -40° to 130°C, the bromine being at such concentrations as to saturate the liquid reaction medium.

3) The process according to claim 2, in which the treatment with bromine is carried out at a temperature from 90° to 110°C.

4) The process according to claim 2, in which the treatment with bromine is carried out at a temperature from 0° to 80°C.

5) The process according to claim 2, characterized in that, in order to obtain a final product having a controlled molecular weight, the product of the photooxidation of C_2F_4 and/or C_3F_6 is subjected to a thermal treatment in order to reduce the peroxide oxygen content to a value pre-established as a function of the desired molecular weight of the final product.

6) The process according to claim 2, characterized in that the UV-radiation photolysis of the oxidation product of C_2F_4 and/or C_3F_6 with bromine is accomplished in the presence of fully fluorinated inert solvents.

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(71) Applicant: Montedison S.p.A.
31, Foro Buonaparte
I-20121 Milan(IT)

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Dr. F. Zumstein Dr. E. Assmann Dipl.-Ing. F. Klingseisen
Bräuhausstrasse 4
D-8000 München 2(DE)

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$$\begin{array}{c}(CFO)\\ |\\ (CF_3)\end{array},$$

statistically distributed along the chain, having a controlled molecular weight and brominated end groups, prepared starting from the product of the photo-chemical oxidation of C_2F_4, and/or C_3F_6, having different peroxide oxygen contents, and subsequent treatment in liquid phase with bromine, at temperatures ranging from −40° to 130°C in the presence of ultraviolet radiations.

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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	EP-A-0 151 877 (MINNESOTA MINING AND MANUFACTURING CO.) * Page 2, line 6, claim 6 *	1	C 08 G 65/00
X	EP-A-0 062 325 (E.I. DU PONT DE NEMOURS & CO.) * Page 21, claim 5 *	1	
A	EP-A-0 089 820 (MONTEDISON)		
A	FR-A-1 585 601 (MONTECATINI)		
A	FR-A-2 008 652 (MONTECATINI)		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 08 G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	13-04-1987	STIENON P.M.E.

CATEGORY OF CITED DOCUMENTS

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